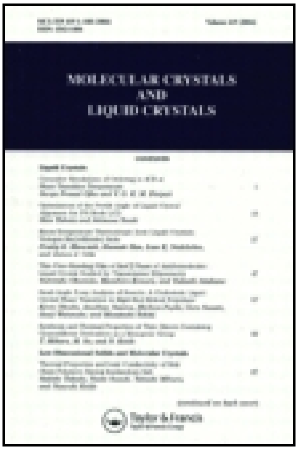

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Pretilted Nematic Layers of 5CB on PTFE Treated Glass Supports

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Version of record first published: 22 Sep 2010

Mol. Cryst. Liq. Cryst., Vol. 465, pp. 301–308, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701206154

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Planar nematic layers of 5CB oriented by "sliding on" nanolayers of PTFE were studied by electrooptic methods. Deposited layers have been characterized by AFM and polarizing videomicroscopy. By using a drop method it was established that the preferred director alignment is tilted opposite to the sliding direction. In some of these samples an unusual modulated domain pattern after switching off a prolonged a.c. excitation was observed for the first time. A possible relation between the domain origin and loosely deposited PTFE layers was suggested.

Keywords: interfaces; liquid crystals; polytetrafluoro-ethylen coating; pretilt angle

Nanometer thick layers of PTFE (Teflon^{TM}) have been deposited on clean glass plates by the method of rubbing a preheated glass by a piece of Teflon [1]. This frictional transfer method uses smooth microscope glass slides as hot substrates. PTFE film was deposited by sliding a solid PTFE bar against the preheated substrate's surface at a 100°C and constant pressure of 130 N/cm^2. Sliding rate was 0.2 cm/s. Deposited layers have been characterized by AFM (PERCEPTION, Assing) in the no contact mode.

This study was performed in the framework of a CNR-BAS joint project. The authors are indebted to Maria DeSanto for AFM characterization.

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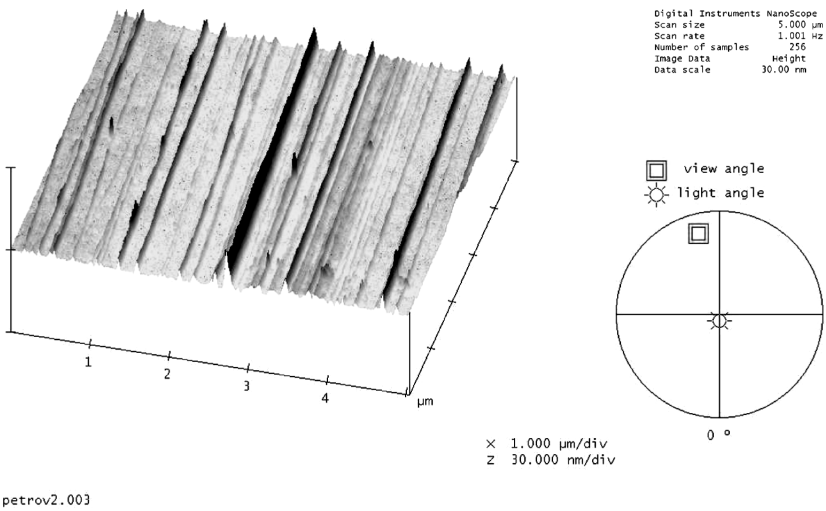

FIGURE 1 3D AFM picture of PTFE on glass. AFM PERCEPTION (Assing) in the no contact mode is employed. The deposition of single PTFE chains of about 4 nm thickness is elucidated.

It was found that elevated temperature produces deposited structures of a substantial thickness, while at 100°C presumably single PTFE chains (4 nm thickness) are deposited (Fig. 1). In the last case well oriented planar layers with some pretilt of nematic PCB are produced.

Optical texture images of nematic droplets placed on PTFE treated glass plates subjected to external electric field were used as a method to determine the pretilt orientation with respect to sliding direction. In general to determine tilt orientation by texture observation one needs to use a second well-defined orienting interface [2,3]. For 5CB is known that a homeotropic anchoring at liquid crystal – air interface take place [4]. In this respect NLC droplets placed on aligning surfaces offer a simplest case of nematic confined between two surfaces. In some previous papers [5,6] it has been demonstrated that drops of NLCs placed on surfaces can indeed form a basis of simple and general methods to characterize the substrates. Determination of the direction of easy axis, the presence of pretilt angle and the tilt direction of NLC molecules has been extracted from disclination line created in the NLC droplets. Advantage of this method is that it can be carried out using not only a small area of alignment surface but also a small amount of NLC. But at the same time the method becomes less sensitive with respect to determination of the tilting direction for small tilt

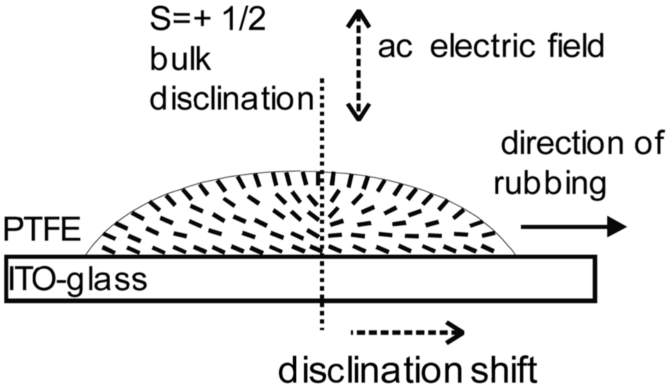

FIGURE 2 Director distribution in the droplet on rubbed PTFE.

angles due to uncertainties in position of the disclination line, which is deposited almost in the droplet center. Here, in order the tilting orientation to become more prominent for registration of small tilt angles, the droplets were additionally subjected to an electric field perpendicular to the droplet substrate. As a result the disclination line was forced to move into opposite direction with respect to the tilting direction (see Fig. 2 and the discussion). The micro decoration displaying by drop method depends strongly on the orientations of the NLC within the droplets, which, in turn, are determined by a balance of effects. These effects include the elastic energy stored in distorted states (bend, twist, or splay) of the NLC, short-ranged interactions between the NLC and the surrounding surfaces (i.e., the anchoring energy), and any externally applied (electric or magnetic) fields.

Polarizing microscopy images of nematic droplets placed on PTFE treated ITO-covered glass plates are shown on Figure 3A and B. A homeotropic anchoring of 5CB at its free surface is assumed [4]. The optical textures formed by droplets of NLC of 4-cyano-4′-pentylbiphenyl (5CB) supported on PTFE covered glass plates were obtained by using the following procedure. First, 5CB was heated to temperature greater than its nematic-to-isotropic transition temperature. Second, several 5CB drops of millimetre size were placed onto the surface of PTFE (warmed above 36°C). The PTFE plate supporting the droplets of 5CB was then transferred to a polarized light microscope and cooled to a nematic phase temperature. In order electric field measurements to be allowed in some cases glass substrates with transparent conductive coating (ITO) were used. After PTFE deposition on a bottom plate parallel glass cells (with a second glass plate facing its ITO-coated side towards the droplet free surface) were assembled. The distance

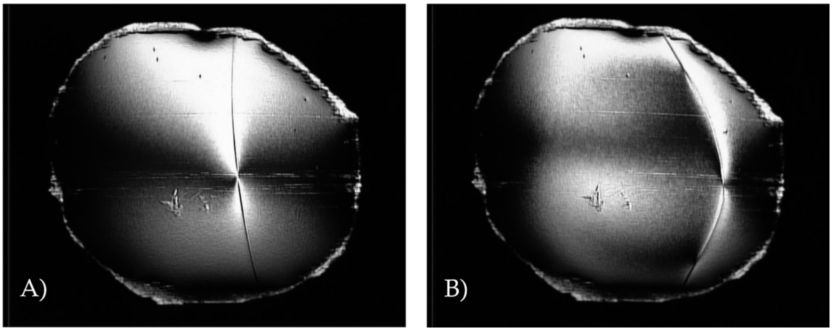

FIGURE 3 Transmission-polarized light image of a droplet of nematic 5CB resting on a PTFE layer: A) a disclination line passing almost trough center of droplet, no electric field; B) disclination line shifted along the rubbing direction under electric field perpendicular to the substrate surface. The direction of sliding deposition of the PTFE film is from left to right. The horizontal dimensions of the images are 2.5 mm.

between the droplet free surface and the ITO-covered top plate was kept by means of a 700 μm Mylar spacer. The optical appearance of the supported NLC drop was imaged by using CCD colour camera TCM 112 (GDS Elettronica) and recorded on a computer.

The relationship between distortions formed within droplets of NLC supported on PTFE surfaces (in the absence and presence of a applied electric field perpendicular to the substrate surface) and properties of the underlying surface is explained on Figure 2.

Figure 3 shows a polarized light micrograph (transmission mode) of a millimeter size droplet of 5CB placed on the orienting surface formed from PTFE. A thin threadlike structure formed along the drop diameter perpendicular to easy molecular direction is observed. It correspond to disclination line of strength $m = +1/2$ which is in consistent with models of distortions observed within droplets of NLCs supported on surfaces reported in [5] where the nematic droplet is anchored parallel to the surface of a substrate with a uniform azimuthal orientation. We conclude, therefore, that the micrographs shown in Figure 3, correspond to uniform, planar anchoring of the nematic on the surface of the PTFE. Homeotropic induced anchoring on free surface and presumably tilted one on PTFE film provide at the two opposite drop edges, lying along the easy direction on substrate two different modes of surface anchoring namely parallel and antiparallel. Thus the disclination line divides nematic droplet into two parts having one of the above mentioned surface modes of orientation. In some of droplets the disclination line appears apparently shifted towards direction coincident with the direction of sliding. Some variations in droplet textures observed could be regarded to PTFE surface anchoring innhomogeneity, which is produced during the PTFE deposition process. In order to establish definitely nematic director distribution inside the droplets and in particular the direction of pretilting orientation ac electric field (80 Hz) along to the glass plate normal was applied. Due to the positive dielectric anisotropy of 5CB under an ac electric field excitation the molecular director starts to reorient towards the surface normal thus favouring the droplet part with pronounced parallel boundary conditions to expand. As a result of the reorientation of the director a disclination line drift was observed. Upon gradual increase of the ac electric field the disclination line shift became more prominent (Fig. 3B). Finally, almost all disclination lines were shifted towards the sliding direction. We interpret these results to indicate that the preferred direction of alignment is tilted opposite to the direction of deposition of PTFE layer (cf. Fig. 2).

Having established the presence of tilt and the tilt sense, we have investigated liquid crystal cells allowing for the excitation of the planar nematic layers by in-plane electric fields. Their glass substrates had PTFE layers only and no ITO layers. They were assembled with the glass plates facing their PTFE-coated sides in an antiparallel tilt configuration and separated by cooper foil of 75 μm serving as electrodes. Electrode distance was 2 mm. Finally the cells were filled with the LC 5CB by capillarity in the isotropic phase and then slowly cooled down to room temperature. In this way uniform planar alignment of the LC imposed by PTFE surface was achieved. Afterwards the cells were placed between crossed polarizers. An electric field parallel to the cell plates directed at a variable angle with respect to crossed polarizers was applied to the nematic cell by means of the copper spacers. These cells were used for investigating dynamics of splay flexoelectric oscillations (to be published elsewhere).

Interestingly, in some of the samples an unusual modulated domain pattern was observed for the first time. It appeared after the layer was first submitted to a prolonged lower frequency field action (for about 30 min or more), followed by a switching off the field. We report on the study of this modulated structure in the present paper. The domain pattern started to grow from a given region of the layer, slowly expanding over the whole layer. It was then memorized for a relatively long time. On the other hand by switching on the longitudinal field, the domain pattern is quickly erased by the orienting action of the positive dielectric anisotropy.

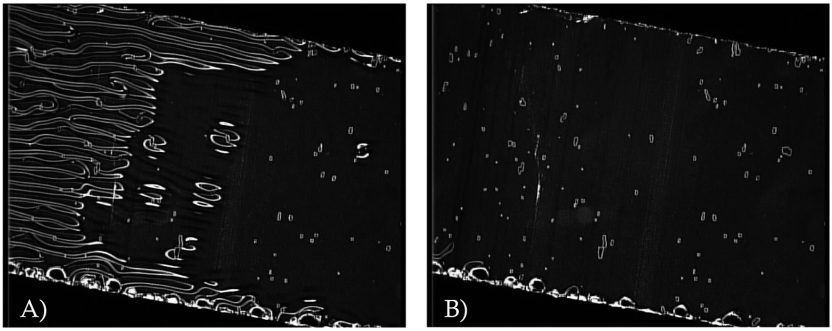

FIGURE 4 Static domains in extinguished position of the nematic layer. Polarizer and analyzer coincide with the edges of the photo frames. A) Nematic 5CB oriented by PTFE layers observed in polarized light after switching off a $150V_{rms}$, 1000 Hz orienting voltage. Domain pattern is growing from left to right, expanding over the whole sample area. The domains are situated perpendicular to easy direction. The upper and lower dark parts are the in-plane electrodes. Thickness of the electrodes is 75 μm and distance between them is 2 mm. B) Erasing of the static domains by an ac voltage of $40V_{rms}$, 1000 Hz. Several immobilized surface disclination lines are visible.

Figures 4 and 5 show the relaxation of static domains in the planar nematic cell at crossed polarizers, either at extinguished or a bright initial orientation of the nematic layer. On Figure 4 two sets of bright lines can be focused at the upper and lower glass plates, indicating some director twist. These surface disclination lines are oriented perpendicular to the rubbing direction and are connected periodically by bulk disclination lines. No core of director discontinuity was observed. Within a few seconds after switching off the orienting electric field spots of strong director fluctuations are formed producing in consequence disclination lines which some times appear as closed loops (see Fig. 4) touching both surfaces and expanding over the whole area.

At room temperature the domains thus formed remained stable for several hours with a weak trend of the sample to restore the initial planar orientation. Finally, after up to 12 hours the samples becomed again planar, with no disclination lines. Another feature is that once the interface conditions have been reached after long flexoelectric excitations it is easily to turn the cells to domain configuration after briefly applying just 40 V (ac or dc) voltage in-plane along the easy direction and then switching it off. The obtained domains after leaving the cell in rest propagate through the nematic layer within several seconds. Approximately the same time is necessary to erase the domains at 40 V by the orienting dielectric torque (positive dielectric

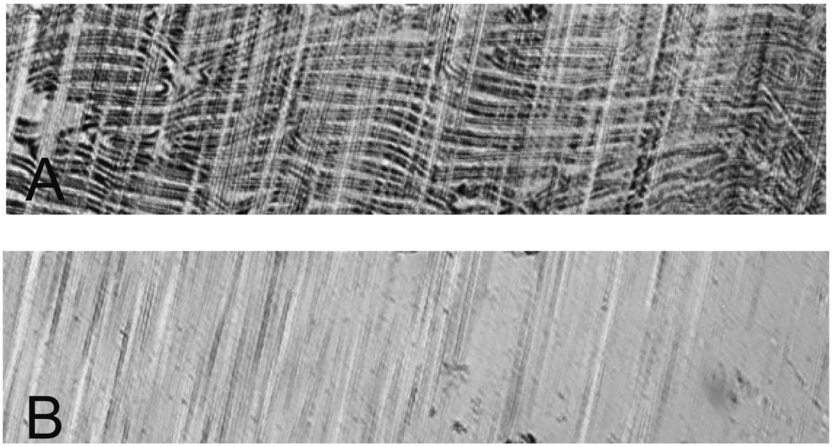

FIGURE 5 Static domains in bright initial position of the nematic layer. Polarizer and analyzer coincide with the edges of the photo frames while the layer is rotated. A) Domain appearance after switching off a $150V_{rms}$, 1000 Hz orienting voltage. B) Erasing of the static domains by an ac voltage of $150V_{rms}$, 1000 Hz.

anisotropy). At higher voltages the erasing process goes much quicker because of the stronger dielectric torques.

Simultaneous action of orienting bulk dielectric forces and splay deforming surface forces seems to lead to the formation of metastable surface anchoring. This mechanism is not fully understood by us now. Plausible qualitative explanation of the further domain formation could be given if a case of loose covered plates is regarded. It is reasonable to be assumed, as in the samples able to form domains many immobilized surface disclination lines are also observed. The presence of such disclination lines is an indication for loose PTFE layer deposition (in agreement with AFM pictures) As a consequence larger pretilt and tilt degeneration could be expected. On the other hand according to [7] nematic layer placed between a rubbed boundary and a free surface with degenerated tilt orientation forms disclination lines perpendicular to the rubbing. To reduce the energy near the core the trajectories of directors escape into the third dimension. The escaped configuration is helical, respectively. The authors conclude from their experiments that a disclination line $s = +1/2$ at degenerated interface exists with its core outside the surface of nematic.

Here we accept that our samples expose similar boundary conditions. Especially at both interfaces we assume for loose PTFE deposition the surface director orientations of $+\theta_0$ and $-\theta_0$ to have equal energy in the plane formed by rubbing direction and surface normal. A possible mechanism of our domain formation could be an escape of director field from a planar, but splayed configuration to a non-planar but twisted configuration (Fig. 4), which is of a lower elastic energy, as the twist elastic constant is lower than the splay one. Therefore, the observed domain pattern should be interpreted as an array of surface disclination lines escaped to the third direction with core outside the surface.

Possible explanation for the following slower return of the nematic layer to the homogeneous planar orientation could be ascribed to evolution in surface anchoring energy. Such evolution in PTFE treated cells has been reported in [8]. The authors observed a slow long-time increasing of the azimuthal anchoring energy calling it an ageing phenomenon.

Important result of this work is the finding of the pretilt angle and the tilt orientation of the nematic director on PTFE films. With some loosely PTFE covered glass substrates an unusual static modulated domain pattern was observed for the first time. These static domains are memorized for several hours. Tentative mechanism of this modulating instability could be an escape of director field from a planar, but splayed configuration to a non-planar but twisted configuration, which is of a lower elastic energy as the twist elastic constant is lower than the splay one. Noteworthy, this study represents the first experimental determination of such properties for PTFE oriented 5CB films.

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